Chapter 8   The Search for "Heavy" Elements

When a nucleus captures a neutron, it often tries to correct for its neutron excess by beta decay, turning a neutron into a proton and thus creating an atom with atomic number Z increased by one unit. This commonly observed phenomenon suggests a way to create new elements of increased atomic number and thus to create ever more massive elements that are not found on Earth. Most of these elements are radioactive, with very short half-lives. However, theories of nuclear structure predict that at a certain atomic number, which is currently beyond present experimental limits, new long-lived nuclei can be created. The known elements are arranged (Fig. 8-1) in a pattern that relates their chemical properties. That arrangement is called the "Periodic Table".

Fig. 8-1. The Periodic Table. The Center for Science and Engineering Education at Lawrence Berkeley National Laboratory provided this table.

The most massive naturally occurring element on Earth is uranium (U), with a nucleus of 92 protons. In 1934, scientists started the search for more massive elements with 93 or more protons. They succeeded in 1940 when neptunium (Np, Z = 93) was synthesized at the University of California, Berkeley. Edwin McMillan and Philip Abelson observed Np while studying fission products produced in the bombardment of ^{238}U with thermal neutrons. They found a radioactive reaction product that was not a fission product. This product was formed by the capture of a neutron to produce ^{239}U, which subsequently β^- decayed to ^{239}Np via the reaction

$$^{239}\text{U} + {}^1\text{n} \rightarrow {}^{239}\text{U} \ (23.5 \ \text{min}) \rightarrow {}^{239}\text{Np} \ (2.36 \ \text{d}),$$
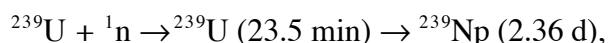
where the half life of the nucleus is indicated in the parenthesis. McMillan and Abelson chemically separated this new element, Np, from the interfering fission products and chemically identified it as neptunium. Since this breakthrough discovery, scientists from all over the world have been trying to discover ever more massive artificially produced elements.

Plutonium (Pu, Z = 94) was discovered in 1941 by bombarding a uranium target with deuterons (a hydrogen nucleus with one proton and one neutron) in the 60-Inch Cyclotron at Berkeley. Glenn Seaborg, Arthur Wahl and Joseph Kennedy chemically separated neptunium from the target and detected alpha particles from the plutonium daughter nuclei, as:

$$^{238}U + {}^{2}H \rightarrow 2\ {}^{1}n + {}^{238}Np\ (2.1\ d) \rightarrow {}^{238}Pu\ (88\ yr)$$

They chemically identified the isotope ^{238}Pu. Then, joined by Emilio Segre, they identified ^{239}Pu and showed that it was fissionable with thermal neutrons.

Once ^{239}Pu was discovered, there was the potential for using it as a new target to produce more massive elements. In 1944 a ^{239}Pu target was bombarded with alpha particles at the 60-Inch Cyclotron to produce curium (Cm, Z = 96) through the following nuclear reaction

$$^{239}Pu\ (24,110\ yr) + {}^{4}He \rightarrow {}^{242}Cm\ (162.8\ d) + {}^{1}n.$$
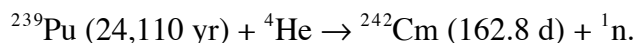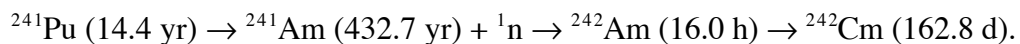
After bombardment the material was sent to the Metallurgical Laboratory at The University of Chicago for chemical separation and identification of the new element. The element ^{242}Cm decays to ^{238}Pu by emitting alpha particles. The identification of curium was possible because the alpha decay of the daughter nucleus, ^{238}Pu, was already known and could be used as a signature for the identification of the curium precursor.

The discovery of americium (Am, Z = 95) soon followed when a ^{239}Pu target was bombarded with thermal neutrons in a nuclear reactor. Plutonium captured several neutrons and ultimately became americium (^{241}Am):

$$^{239}Pu\ (24,110\ yr) + {}^{1}n \rightarrow {}^{240}Pu\ (6,564\ yr) + {}^{1}n \rightarrow {}^{241}Pu\ (14.4\ yr)$$

and
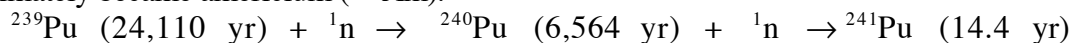
$$^{241}Pu\ (14.4\ yr) \rightarrow {}^{241}Am\ (432.7\ yr) + {}^{1}n \rightarrow {}^{242}Am\ (16.0\ h) \rightarrow {}^{242}Cm\ (162.8\ d).$$

Americium was chemically separated from plutonium and further identified by observing its beta decay to the known ^{242}Cm isotope.

Once americium and curium were found and isolated in macroscopic amounts, they were used as targets to produce more massive elements through particle bombardments. Berkelium (Bk, Z = 97) was produced by bombarding milligram quantities of americium with helium ions,

$$^{241}Am\ (432.7\ yr) + {}^{4}He \rightarrow {}^{243}Bk\ (4.5\ h) + 2\ {}^{1}n.$$
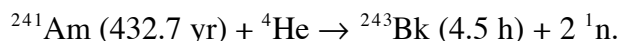
Rapid chemical techniques were developed in order to separate and identify this new short-lived element. Likewise, californium (Cf, Z = 98) was produced in a helium bombardment of a target made of microgram amounts of curium by

$$^{242}\text{Cm (162.8 d)} + {}^{4}\text{He} \rightarrow {}^{245}\text{Cf (45 min)} + {}^{1}\text{n}.$$
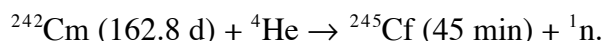
The identification of this element was accomplished with only the 5000 atoms produced in this experiment. The next two elements, einsteinium (Es, Z = 99) and fermium (Fm, Z = 100), were unexpectedly found in the debris from the "Mike" thermonuclear explosion that took place in the Pacific Ocean in 1952. Debris from the explosion was collected and analyzed at several laboratories, and the new elements were discovered in chemical separations of the material. Scientists explained the production of einsteinium and fermium through multiple neutron captures by the uranium used in the thermonuclear device followed by several successive beta decays, which ultimately resulted in atoms with atomic numbers 99 and 100.

The last three elements in the actinide series are mendelevium (Md, Z = 101), nobelium (No, Z = 102) and lawrencium (Lr, Z = 103). Mendelevium was truly a unique discovery because the new element was produced and identified virtually one atom at a time. Einsteinium was bombarded with helium ions to produce mendelevium through:

$$^{253}\text{Es (20.5 d)} + {}^{4}\text{He} \rightarrow {}^{256}\text{Md (78.1 min)} + {}^{1}\text{n}.$$
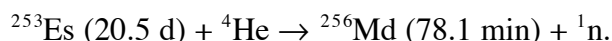
The production of mendelevium was estimated to be only a few atoms per experiment. The reaction products from the bombardment were collected on thin gold foils that were dissolved in an acid solution, and then chemically treated in order to separate and identify the Md atoms. This is commonly called the recoil method, and is used when small numbers of atoms are produced.

The discovery of nobelium was controversial. A team of scientists from several different laboratories claimed discovery in 1957. However, scientists from the United States and the Soviet Union could not confirm their findings. The original claim was proven to be false; the product that was thought to be nobelium was actually something completely different. Nobelium was finally produced and positively identified in 1958 through the following reaction:

$$^{246}\text{Cm (4730 yr)} + {}^{12}\text{C} \rightarrow {}^{254}\text{No (55 s)} + 4\ {}^{1}\text{n}.$$
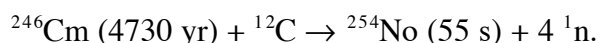
The first identification of lawrencium was made at the Berkeley Laboratory's Heavy Ion Linear Accelerator (HILAC) in 1961. Several targets of californium isotopes were bombarded with beams of boron. The reaction products were collected on a Mylar tape and moved past a series of alpha detectors. The element lawrencium was identified on the basis of the known alpha decays of its descendant nuclei.

By observing the decay chain of their descendant nuclei, scientists discovered elements 104 through 112. Only a few atoms of these new elements were produced in each experiment. The atoms were isolated from the target and beam material by using a particle separator, which separates atoms, based on their different masses. The atoms were then allowed to decay and the subsequent alpha particle decay products from the descendant nuclei were correlated to identify the unknown parent nucleus. In the identification of element 112, the decay chains of parent-daughter-granddaughter nuclei (Fig. 8-2) identified the individual atoms. Different combinations of target and projectile were used in accelerators to produce these new elements.
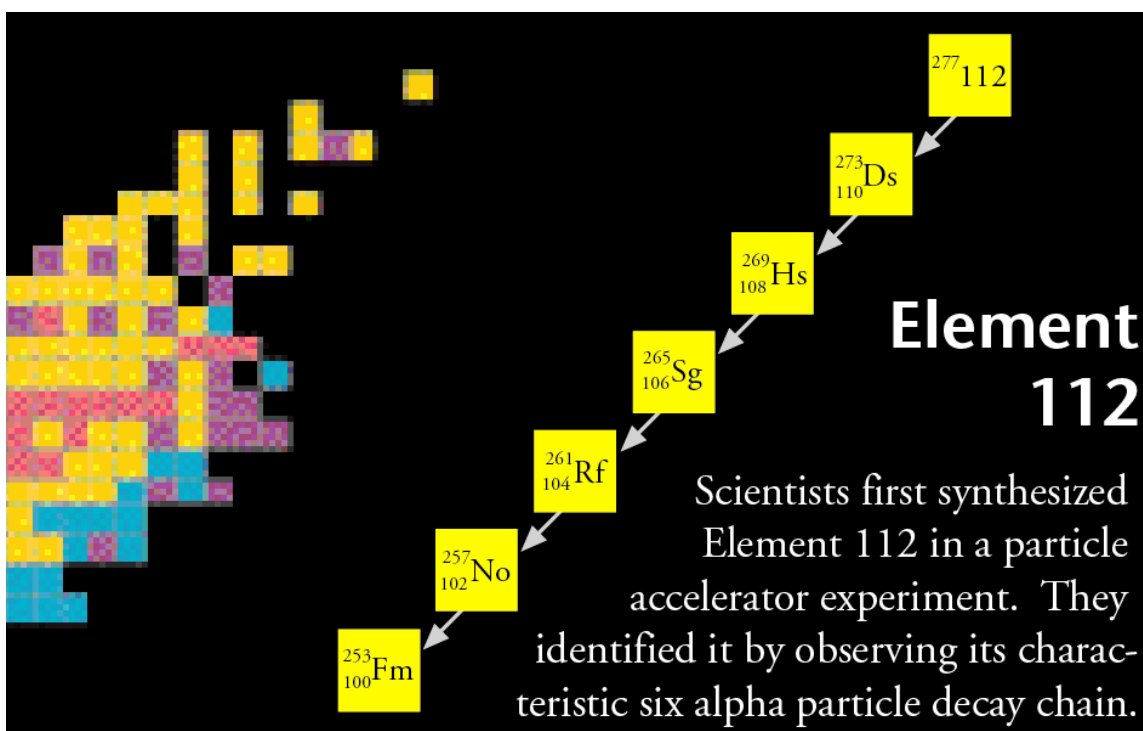
Fig. 8-2. The decay chain for identifying element 112. Element 112 has not yet been officially sanctioned a recognized element.

Rutherfordium (104), dubnium (105), and seaborgium (106) were synthesized and identified at Berkeley. Bohrium (107), hassium (108), and meitnerium (109) were synthesized and identified in the early 1980s at the Gesellschaft für Schwerionenforschung (GSI) laboratory near Darmstadt, Germany. In the 1990s, unnamed element 110 was identified at the GSI, Berkeley, and Dubna laboratories, and elements 111 and 112 were found at the GSI laboratory.

Traditionally, the discoverers of a new element chose its name, and then the International Union of Pure and Applied Chemistry (IUPAC) officially approves it. Table 8-1 lists the currently approved IUPAC names. Recently, IUPAC gave credit for the synthesis of element 110 to the GSI group and then invited them to propose a name.! The GSI group proposed the name darmstadtium with symbol Ds after the place in Germany where the element was discovered.! In 2003, darmstadtium became the official name of element 110. In 2003, the committee recognized that GSI discovered element 111, but declared there is insufficient evidence for claiming the discovery of element 112. As of this publication, no name has been proposed for element 111.

In 1999, a team of scientists working at the Flerov Laboratory in Russia announced that they found element 114 with a lifetime of 30 seconds. There have been other claims for discoveries of elements above 112. Some have been withdrawn. All assertions for the discovery on an element need independent confirmation. Until, scientists are persuaded that the discoveries for elements above 111 are valid, they will not be named.

Table 8-1. "Heavy" element names that are approved by IUPAC.

Element Number	IUPAC Proposal	Symbol
101	Mendelevium	Md
102	Nobelium	No
103	Lawrencium	Lr
104	Rutherfordium	Rf
105	Dubnium	Db
106	Seaborgium	Sg
107	Bohrium	Bh
108	Hassium	Hs
109	Meitnerium	Mt
110	Darmstadtium	Ds

New experimental techniques and apparatus have been developed for scientists to extend the periodic table to even more massive elements. A more efficient particle separator uses magnetic fields to separate atoms based on their mass and charge. This equipment can detect nuclides with low production rates and extremely short half-lives The present limits for discovering new elements are based on the low production rates and short half-lives. The hope is that new development in detection equipment will increase the sensitivity for detecting fewer atoms (or even a single atom) with very short half-lives. A widely used theory predicts the existence of elements up to $Z = 125$. In this model, more massive elements would be so unstable that their nuclei would immediately fly apart into nucleons and nuclear fragments and never become atoms.

It has been possible to study the chemical properties on the macroscopic scale for elements as massive as einsteinium (element 99) and on the tracer scale for elements as massive as seaborgium (element 106). The elements beyond the actinides in the Periodic Table are termed the "transactinides" and are shown in a Modern Periodic Table, Fig. 8-1, in their expected places. The yields of the most massive elements produced in bombardments of target nuclei with "heavy" ions become extremely small with increasing atomic number, dropping to as little as one atom per week of bombardment for elements as massive as atomic number 112. The half-lives decrease into the millisecond and the microsecond range so that identification of the new nuclei becomes increasingly difficult. Their half-lives would be impossibly short were it not for the presence of closed shells of nucleons to increase the nuclear stability.

Table 8-2. Summary of the reactions and methods used in the discovery of the actinide and transactinide elements. See Chapter 7 for an explanation of the reaction notation.

Element	Production Reaction(s)[1]	Method of Discovery	Year
neptunium (Np)	$^{238}U(n,\beta^-)^{239}Np$	Chemical Separation	1940
plutonium (Pu)	$^{238}U(^2H,2n)^{238}Np$ $^{238}Np(\beta^-)^{238}Pu$	Chemical Separation	1941
curium (Cm)	$^{239}Pu(^4He,n)^{242}Cm$	Chemical Separation	1944
americium (Am)	$^{239}Pu(n,\gamma)^{240}Pu$ $^{240}Pu(n,\gamma)^{241}Pu$ $^{241}Pu(\beta^-)^{241}Am$	Chemical Separation	1945
berkelium (Bk)	$^{241}Am(^4He,2n)^{243}Bk$	Chemical Separation	1949
californium (Cf)	$^{242}Cm(^4He,n)^{245}Cf$	Chemical Separation	1950
einsteinium (Es)	$^{238}U(15n,7\beta^-)^{253}Es$	Chemical Separation[2]	1952
fermium (Fm)	$^{238}U(17n,8\beta^-)^{255}Fm$	Chemical Separation[2]	1953
mendelevium (Md)	$^{253}Es(^4He,n)^{256}Md$	Recoil Method, Chemical Separation	1955
nobelium (No)	$^{246}Cm(^{12}C,4n)^{254}No$	Recoil Method, Chemical Separation	1958
lawrencium (Lr)	$^{249/250/251/252}Cf(^{10/11}B,xn)^{258}Lr$	Direct α Counting[3]	1961
rutherfordium (Rf)	$^{249}Cf(^{12}C,4n)^{257}Rf$ $^{249}Cf(^{13}C,3n)^{259}Rf$	Parent-Daughter α Correlation	1969
dubnium (Db)	$^{249}Cf(^{15}N,4n)^{260}Db$	Parent-Daughter α Correlation	1970
seaborgium (Sg)	$^{249}Cf(^{18}O,4n)^{263}Sg$	Parent-Daughter-Granddaughter α Correlation	1974
bohrium (Bh)	$^{209}Bi(^{54}Cr,n)^{262}Bh$	Velocity Separator[4]	1981
hassium (Hs)	$^{208}Pb(^{58}Fe,n)^{265}Hs$	Velocity Separator[4]	1984
meitnerium (Mt)	$^{209}Bi(^{58}Fe,n)^{266}Mt$	Velocity Separator[4]	1982
darmstadtium (Ds)	$^{209}Bi(^{59}Co,n)^{267}Ds$ $^{208}Pb(^{62,64}Ni,n)^{269,271}Ds$ $^{244}Pu(^{34}S,5n)^{273}Ds$	Mass Separator Velocity Separator[4,5] Recoil Separator	1991 1994 1995
111 (to be named)	$^{209}Bi(^{64}Ni,n)^{272}111$	Velocity Separator[4]	1994
112 (unnamed)	$^{208}Pb(^{70}Zn,n)^{277}112$	Velocity Separator	1996

[1]When more than one reaction is given, it means that a sequence of reactions was necessary to discover the element.

[2]The Es and Fm reactions were not done in a laboratory setting; multiple neutron captures, followed by successive beta decays were the result of a thermonuclear explosion.

[3]A mixture of four Cf isotopes was bombarded simultaneously with a beam containing ^{10}B and ^{11}B. The symbol "xn" means that different numbers of neutrons were emitted, depending on the actual combination of target and beam used to produce Lr.

[4]A velocity separator is used to separate reaction products based on the fact that reaction products of different masses will be emitted with different velocities.

[5]At GSI two different reactions were used to produce two different isotopes of element Ds.

It has been possible to study the chemical properties of rutherfordium, hahnium and seaborgium using the advanced techniques of one-atom-at-a-time chemistry. These experiments show that these properties generally are consistent with those expected on the basis of extrapolation from those of their lower-mass *homologues* in the Periodic Table, hafnium, tantalum, and tungsten. Recent studies have shown that the properties of bohrium (107) and hassium (108) are the homologues of rhenium and osmium. However, the chemical properties cannot be determined reliably in detail from trends exhibited by the lighter homologues, because of the important role played by relativistic effects (the fact that some electrons are moving at velocities near the speed of light) in these more massive elements. Elements higher than hassium are placed in their expected place in the Periodic Table.

It will surely be possible to study the macroscopic properties of fermium (element 100) and not out of the question that this will eventually be done for mendelevium (element 101). The art of one-atom-at-a-time chemistry will advance far beyond what can be imagined today to make it possible to study the chemistry of most massive elements. All of this will result in the delineation of relativistic effects on the chemical properties of these very massive elements, which might thus be substantially different from those expected by simple extrapolation from their less massive homologues in the Periodic Table.

Books and Articles:

G. T. Seaborg and W. D. Loveland, *The Elements Beyond Uranium*, John Wiley and Sons, Inc., New York (1990).

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M. Schädel et al., *Chemical Properties of Element 106 (seaborgium),* Nature **388**, 55 (1977).

P. J. Karol et al., *On the Discovery of elements 110-112,* Pure Appl. Chem., 73, 959-967 (2001).